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TRITERPENES FROM THE LEAVES OF *RHODODENDRON CINNABARINUM* HOOK. F.

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ABSTRACT

Petroleum ether extract of the leaves of *Rhododendron cinnabarinum* Hook. f. has yielded seven triterpenes of which five have been identified as friedelin, *epi*-friedelinol, α-amyrin, campanulin and ursolic acid occurring in 0.05, 0.08, 0.12, 0.02 and 0.3% respectively. A neutral triterpene m.p. 226° and an acidic triterpene (methyl ester m.p. 232°) have also been obtained in 0.01 and 0.007% yields respectively, characterisations of which are in progress.

Although various species of *Rhododendron* (Family: *Ericaceae*) available in India are recently being chemically examined[1-4], no work has so far been made on *R. cinnabarinum* Hook. f. The present work deals with the triterpene contents of the leaves of this plant. The petroleum ether extract of the leaves has been separated into acidic and neutral fractions. The acidic fraction has been esterified with diazomethane. The methyl esters of the acidic triterpenes as well as the crude neutral triterpenes have been separately chromatographed and the different constituents obtained therefrom have been characterised by comparison with authentic samples. It has been possible to identify the following triterpenes from leaves of *R. cinnabarinum*: α-amyrin and ursolic acid (of α-amyrin series), friedelin and *epi*-friedelinol (of friedelin series) and campanulin (of glutinane series). Campanulin, an oxide—bridged glutinane, $C_{30}H_{50}O$, m.p. 204° has so far only been reported from some species of *Rhododendron* 2, 4, 5. This was earlier described by Arthur and Hui as *epoxy*-glutinane isolated from *R. westlandii* but the present author prefers the use of the name campanulin for the compound. Ursolic acid is almost an universal constituent of this genus (*Rhododendron*) and although friedelin, *epi*-friedelinol and campanulin have been reported in some of the species, alone or together, α-amyrin appears to be first recorded in the present study.

EXPERIMENTAL

(Optical rotations have been examined in chloroform solution and the m.p.s are uncorrected.)

2.5 kg. of powdered air-dried leaves were exhaustively extracted in a Soxhlet apparatus with petroleum ether (b.p. 60-80). The petroleum ether on evaporation yielded a semi-solid mass (24.5 g.). This was dissolved in 2500 c.c. ether and the ethereal solution repeatedly extracted with 5% aqueous sodium hydroxide solution. The ether layer was washed free from alkalies, dried over anhydrous sodium sulphate and evaporated. The neutral fraction thus obtained weighed 15.1 g. The alkaline aqueous solution was acidified with hydrochloric acid and filtered. The residue on drying weighed 9.4 g.

Examination of the acidic fraction—The crude acidic fraction was esterified with diazomethane in ethereal solution and the methyl ester (11.2 g.) dissolved in benzene (100 c.c.) was chromatographed over Brockman alumina (14″ × 1.5″).

Table I

Chromatography of methyl ester

Fraction	Solvent	Volume	Residue
1-42	Petroleum ether (60-80): benzene; 1:1	50 c.c. each	Nil
43-51	Benzene	-do-	White crystals m.p. 152-63°
52-107	-do-	-do-	Nil
108-114	Ethyl acetate	-do-	Nil
115-117	-do-	-do-	White crystals m.p. 220-26°
118-165	-do-	-do-	Nil

Fractions (43-51): Isolation of methyl ursolate—These were mixed together and repeatedly crystallised from dilute alcohol (50%) when fine silky needles separated (yield 7.8 g.), m.p. 168°; $[\alpha]_D$ +58.4°. It responded strongly to Liebermann-Burchardt reaction and gave a distinct yellow coloration with tetranitromethane. Acetyl derivative of above was prepared by heating 100 mg. of the ester with 2 c.c. pyridine and 3 c.c. acetic anhydride on a water bath for 2 hrs. and working up as usual. It crystallised from dilute methanol, m.p. 245-47°. The physical constants of the ester and its acetate closely agreed with those of methyl ursolate and its acetate. Mixed m.p. of the ester with an authentic sample remained undepressed.

The major acidic constituent of the petroleum ether extract of the leaves was thus proved to be ursolic acid.

Fractions (115-117)—These were mixed together and crystallised from dilute alcohol (yield 0.18 g.) in fine needles, m.p. 232°; $[\alpha]_D$+41.7°. It responded to Liebermann-Burchardt reaction and produced yellow coloration with tetranitromethane.

Attempts are being made to collect the material in larger quantities to facilitate its characterisation.

Examination of the neutral fraction—The neutral triterpenes (15.1 g.) dissolved in 50 c.c. benzene were adsorbed on a column (18″ × 2″) of Brockman alumina and eluted with different solvents.

TABLE II

Chromatography of neutral triterpenes

Fraction	Solvent	Volume	Residue
1-5	Petroleum ether (60-80)	250 c.c. each	Red oil with crystals.
6-7	-do-	-do-	Nil
8-17	-do-	-do-	White crystals m.p. 232-48°.
18-40	-do-	-do-	Nil
41-116	-do-	-do-	White crystals m.p. 169-73°.
117-149	-do-	-do-	Nil
150-214	Benzene	250 c.c. each	Nil
215-216	-do-	-do-	Small quantity of crystals m.p. 216-24°.
217-232	-do-	-do-	Nil
232-233	-do-	-do-	White crystals m.p. 269-72°.
234-314	-do-	-do-	Nil
315-375	Ethyl acetate	-do-	Nil

Fraction (1-5): *Isolation of campanulin*—These were mixed together and repeatedly crystallised from large volumes of acetone when fine colourless needles were obtained (yield 0.5 g.), m.p. 208° ; $[\alpha]_D$ +72.5°. It responded to Liebermann-Buchardt reaction and did not give any coloration with tetranitromethane. Attempts to prepare an oxime or an acetate were abortive. This compound although of a higher m.p. (208°) appeared to be *epoxy*-glutinane, m.p. 202° of Arthur and Hui and a mixed m.p. determination with their sample showed to depression. This compound was therefore identified as campanulin (*epoxy*-glutinane).

Fractions (8-17): *Isolation of friedelin*—On crystallisations from a mixture of chloroform and ethyl acetate fine colourless needles were obtained (yield 1.3 g.), m.p. 256-62° ; $[\alpha]_D$ − 27.6°. It responded to Liebermann-Burchardt reaction but was indifferent towards tetranitromethane. The oxime of the compound was prepared by refluxing 100 mg. of it dissolved in 10 c.c. pyridine, 200 mg. of hydroxylamine hydrochloride and 2-3 c.c. absolute alcohol on water bath for 3 hours. On cooling some crystals separated out. These were filtered and crystallised from benzene-methanol mixture, m.p. 288-90°.

The ketone and its oxime agreed closely with friedelin and its oxime in their physical constants. Mixed m.p.s. of both with authentic samples were determined and found to remain undepressed. So the compound was identified as friedelin.

Fractions (41-116): *Isolation of α-amyrin*—All were mixed together and crystallised from methanol (yield 3.1 g.) ; m.p. 186° ; $[\alpha]_D$ +81°. It responded to Liebermann-Burchardt test and gave yellow coloration with tetranitromethane. The acetyl derivative crystallised from alcohol, m.p. 224°. The identity of the alcohol with α-amyrin was established by mixed m.p. determination with an authentic sample which showed no depression.

Fractions (215-16)—These on repeated crystallisations from methanol gave fine needles, (yield 0.25 g.), m.p. 226° ; $[\alpha]_D$ +66.7°. It responded to Liebermann-Burchardt test and produced yellow coloration with tetranitromethane.

Attempts are being made to procure the material in quantity.

Fractions (232-33): *Isolaltion of epi-friedelinol*—On crystallisations from chloroform fine glistening plates were obtained, (yield 2.06 g.), m.p. 273-74°, $[\alpha]_D$ +20.4°. It responded to Liebermann-Burchardt test but did not produce any coloration with tetranitromethane. The acetate crystallised from benzene-methanol mixture, m.p. 282-85°.

A mixed m.p. determination of the alcohol with *epi*-friedelinol remained undepressed.

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